PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method of Regenerating Spent Liquors produced in the Pickling of Iron or Steel Products

We, METALURSKI INSTITUT, of 3, Jamova, Ljubljana, Yugoslavia, a Yugoslav Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that very large amounts of sulphuric acid are consumed in the pickling of iron or steel products, for example in sheet or strip form. It is true that the known pickling processes have to a large extent exhausted the acid used for pickling; nevertheless no further economic use can be found for the spent pickling liquor, which still contains from 3 to 5 parts by weight of sulphuric acid (H_2SO_4). In the case of modern rapid continuous pickling processes, however, the used pickling liquor still contains as much as 10 to 18 parts by weight of sulphuric acid, which it would be uneconomic to discard. In any case the spent pickling liquor contains larger or smaller amounts of dissolved ferrous sulphate ($FeSO_4$), it has hitherto been customary to crystallise this out from the pickle by evaporation and subsequent water-cooling and then separating it, for example by centrifuging.

With the steadily increasing output of the iron industry, pickling installations have also increased in extent, particularly those using the continuous pickling process for sheet and strip products. The difficult problem consequently becomes more insistent as to what use can best be made of the large amounts of ferrous sulphate ($FeSO_4$) produced in the pickling process and the free sulphuric acid still contained in the spent pickling solution. In addition, the standards imposed with respect to purity of the waste liquors are becoming stricter, and such discarded liquors must of course not contain any sulphuric acid or sulphates, as these substances attack concrete and iron structures, and destroy fauna and flora in the water.

Various proposals have been offered for solving the problem. A method is known, for example, by which the sulphuric acid is regenerated from the ferrous sulphate by treatment with hydrochloric acid. Still other, prior methods are based on the principle of working up the ferrous sulphate into iron oxides and sulphur dioxide, which is further worked up into sulphuric acid. All these methods prove in practice either too costly or else insufficient.

The present invention relates to a new method for regenerating the spent pickling liquor produced in the pickling of iron or steel products, and is chiefly characterised by the fact that the ferrous sulphate in the exhausted pickling solution from the pickling plant is separated out in crystalline form as ferrous sulphate-heptahydrate ($FeSO_4 \cdot 7H_2O$) by cooling to —12° C. to —16° C. In the process some 75% of the ferrous sulphate present in the used liquor is recovered. After separating off this quantity of ferrous sulphate-heptahydrate, for example by centrifuging or filtering, a spent lye remains which is poorer in iron but which still contains considerable amounts of sulphuric acid—namely, in the case of continuous pickling, for example 15 parts by weight—and which, when a corresponding amount of fresh sulphuric acid has been added, can be re-used for the pickling process.

In order to be able to recover iron and sulphuric acid as such, from the separated ferrous sulphate-heptahydrate, after renewed solution in water and precipitation with sodium hydroxide and air oxidation, iron oxides ar iron oxide-hydrates and a sodium sulphate solution are obtained. The iron oxides or oxide-hydrates are separated from this solution, for example by filtration. The

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sodium sulphate solution obtained, having been enriched with solid sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) which is produced in the subsequent production stage, is worked up in a manner known *per se* by electrolysis into sodium lye (NaOH) and into a solution of sodium sulphate (Na_2SO_4) and sulphuric acid. The caustic soda solution thus obtained is used for fresh precipitation of iron oxides or oxide-hydrates from the iron sulphate solution continuously supplied.

The solution of sulphuric acid and sodium sulphate resulting from the electrolysis nevertheless has too low a concentration of sulphuric acid and too high a concentration of sodium sulphate to be employed for enriching the spent lye as obtained after separation of the ferrous sulphate-heptahydrate from the used pickling solution. On the other hand it contains such quantities of sodium sulphate as would be damaging to the pickle, if it were to be re-used in the regenerated pickle. The sodium sulphate is accordingly crystallised out, by cooling to −8° C. from the sulphuric acid and sodium sulphate solution which was obtained in the electrolysis, in the form of crystalline sodium sulphate decahydrate ($Na_2SO_4.10H_2O$), which is separated for example by filtration or centrifuging. This crystalline sodium sulphate decahydrate is used for enriching the sodium sulphate solution which remains after precipitation and separation of the iron oxides or iron oxide-hydrates and which is then to be treated by electrolysis.

In this way, over 80% of the sodium sulphate present has been extracted from the sulphuric acid and sodium sulphate solution produced in the electrolysis and the sulphuric acid concentration itself has been raised to 15 to 18 per cent by weight. As this solution, by reason of its insufficient acid concentration, cannot be used as such for regenerating the first spent liquor from which the major portion of iron sulphate had previously been separated, the said acid is first mixed with the said spent liquor, whereupon the excess proportion of water, namely 25 to 30%, is taken off by freezing out at −15 to −20° C. in the form of small ice crystals in accordance with an otherwise known process and these small ice crystals are thereafter separated by centrifuging, filtration, etc., and used for cooling the exhausted pickle and for dissolving the ferrous sulphate-heptahydrate before the precipitation with caustic soda solution. The solution remaining after the water has been frozen out contains about 20 per cent by weight or more of sulphuric acid and contains ferrous sulphate and sodium sulphate in such low proportions as to enable the said solution to be returned to the pickling process as fresh pickle.

In accordance with the present invention, the advantage of the new method lies in the fact that the regeneration of the spent pickle is complete and this regeneration can be carried out in a cyclic process without evaporation or the application of elevated temperatures, while on the other hand the cooling necessary to the new method can be carried out with the aid of simpler apparatus and demands a low consumption of energy.

WHAT WE CLAIM IS:—

1. A method of regenerating spent liquors produced in the pickling of iron or steel products, with sulphuric acid, comprising separating a substantial part of the ferrous sulphate ($FeSO_4$) contained in the pickling liquors by supercooling to −12° C. to −16° C. as crystalline ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), dissolving the separated crystalline ferrous sulphate heptahydrate in water, precipitating the iron as iron oxide or iron oxide-hydrate with sodium hydroxide solution (NaOH) and oxidation by air, filtering the remaining solution enriched with additional sodium sulphate decahydrate ($NaSO_4.10H_2O$), subjecting the solution to electrolysis thereby forming on the one hand a first solution of sulphuric acid (H_2SO_4) and sodium sulphate (Na_2SO_4) and on the other hand a second solution containing sodium hydroxide; cooling the first solution cooling to under −8° C. and separating sodium sulphate decahydrate therefrom leaving a solution rich in sulphuric acid and poor in sodium sulphate; adding this sulphuric acid solution to the spent liquor obtained after the initial separation of ferrous sulphate to reconstitute pickling liquor; and utilising the second solution for precipitation of the iron as iron oxide or iron oxide-hydrate.

2. A method as claimed in Claim 1, wherein the sodium sulphate decahydrate which is separated from the cooled first solution, is used as the additional sodium sulphate decahydrate for enriching the sodium sulphate solution formed in the conversion of the ferrous sulphate into iron oxide or iron oxide-hydrate.

3. A method as claimed in Claim 1 or 2, wherein the solution which is rich in sulphuric acid and poor in sodium sulphate is mixed with the spent liquor obtained by separation of the ferrous sulphate, and the mixture is cooled to −15° C. to −20° C., whereupon 25% to 30% of the water present is separated as small ice crystals from the mixture by filtration or centrifuging, while the residual solution obtained is used as fresh pickling liquor.

4. A method of regenerating spent liquors produced in the pickling of iron or steel products, with sulphuric acid, substantially as described.

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